

“In situ” Raman Characterization of Poly(5-amino 1-naphthol)

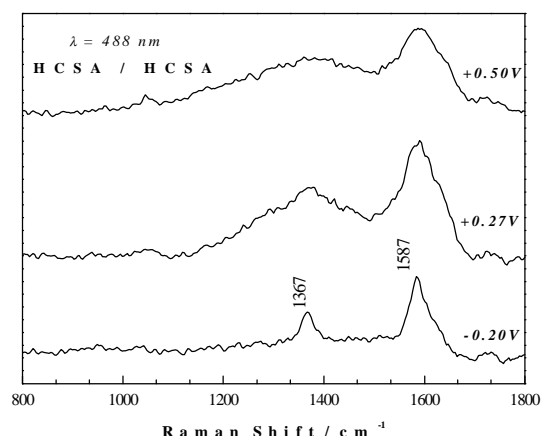
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Intrinsically conducting polymers (ICP) have the possibility of combining the intrinsic properties of the plastic with the electrical, magnetic and optical characteristics of metals and semiconductors. Among the possible applications of this materials it can be pointed out : rechargeable batteries, electronic devices, sensors, biosensors, electrochromic devices, light emitting diodes, active protection to corrosion, blindage, etc. A new series of conducting polymers can be electropolymerized from naphthol derivatives. Recently, Pham et al. [1,2] have reported the synthesis of electroactive polymers of 5-amino 1-naphthol, which have the particularity of containing two functional groups :  $-\text{NH}_2$  and  $-\text{OH}$ ; that can be electrochemically oxidized. It is known that, in basic media, the polymerization occurs through the oxidation of the  $-\text{OH}$  group; on the contrary, in acid media, polymerization occurs by the electrooxidation of the  $-\text{NH}_2$  group, resulting in an polyaniline-like structure.

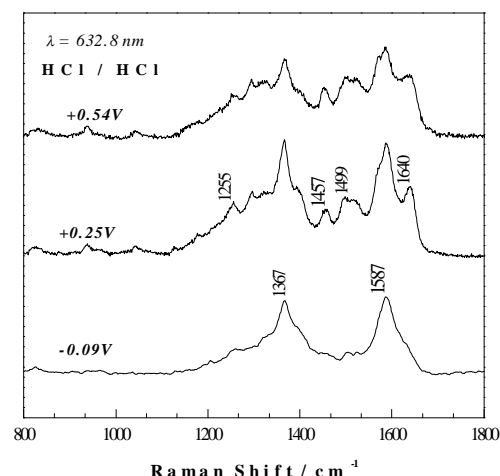
The aim of this paper is to study the electrochemical polymerization of 5-amino 1-naphthol, in different acids : HCl,  $\text{HClO}_4$ , HCSA (10-camphorsulfonic acid) and PTSA (p-toluenesulfonic acid); and thereafter to characterize “in situ” by Raman spectroscopy.

The electrochemical synthesis was carried out in  $1 \text{ mol.L}^{-1}$  (HCl or HCSA) aqueous solutions with 5-amino 1-naphthol ( $1.10^{-3} \text{ mol.L}^{-1}$ ), by applying a potential scans from 0.0 to 0.90V in the two first cycles and from 0.0 to 0.70 vs. Ag/AgCl on the others at a  $50 \text{ mV.s}^{-1}$  sweep rate. The accumulated charge in each film was, approximately,  $3.10^{-3} \text{ C}$  and films were deposited onto Pt or Au substrates and placed in an electrochemical cell containing free monomer electrolytic solutions. In situ Raman spectra were recorded in a Renishaw Raman Imaging System 3000 containing an Olympus metallurgical microscope and a CCD detector. Two exciting radiations were used : 632.8 and 488 nm. Laser power was kept below 0.7 mW to avoid sample degradation.

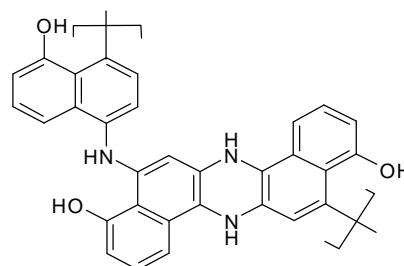
Figure 1 shows Raman spectra obtained with the 488 nm exciting radiation. When the film is the reduced state, two bands located at 1583 and  $1363 \text{ cm}^{-1}$ , can be observed. When potential is increased the band at 1583



presents an enlargement to lower frequencies and a shoulder at  $1640 \text{ cm}^{-1}$ . In the region corresponding to  $1367 \text{ cm}^{-1}$ , the appearance of other non well-defined bands can also be observed. Previous studies[3] had attributed the band at  $1583 \text{ cm}^{-1}$  to the C=C stretching of naphthalene ring and the band at  $1367 \text{ cm}^{-1}$  to C-H bending[4]. It is important to note that these bands do not change in intensity with potential. Figure 2 shows Raman spectra obtained with the 632.8 nm exciting radiation and it can be noted that drastic changes occur with potential.



When potential is raised, other bands in the 1200 to  $1650 \text{ cm}^{-1}$  appear. The band at 1255 is assigned to C-N stretching and those observed in the 1280 to  $1330 \text{ cm}^{-1}$  region are related to semiquinone species (polaronic species). The bands associated to C=N modes, related to the oxidation of the polymer, appear in 1457 and  $1500 \text{ cm}^{-1}$ . The band observed at  $1640 \text{ cm}^{-1}$  is controversial due to the fact that it has been associated to imine groups but the frequency is very high for a “polyaniline-like” structure that some authors claimed[1,2]. On the other hand, if a “ladder” type polymer is formed during polymerization due to coupling in the “ortho” position, this band could be attributed to C-N-C stretching. Figure 3 shows the chemical scheme of this possible “ladder” structure:



The “in situ” investigation unambiguously indicates that all spectral changes are related to different oxidation states of the polymeric chain and that the electrolytic medium will interfere in the intensity of these changes.

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References:

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